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New p–n diblock and triblock oligomers: effective tuning of HOMO/LUMO energy levels

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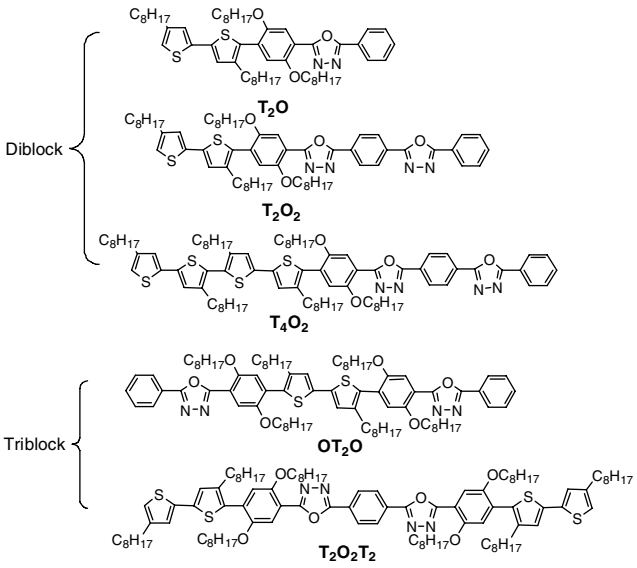
Abstract—A new series of oligomers consisting of thiophene as p-type unit and oxadiazole as n-type unit were synthesized, and their photophysical and electrochemical properties were evaluated. Cyclic voltammography studies demonstrated that the electronic properties of the p–n diblock oligomers could be modulated by changing the number of thiophene and oxadiazole rings. The molecular regiochemical effect to the electrochemical and optical properties was also investigated.

As potential patterned light sources and large area displays, polymer light-emitting diodes (PLEDs) have drawn special attention.[1] High efficiency single-layer PLEDs require the conjugated polymers with balanced injection and transport properties for both electrons and holes.[2] In our previous work, we have developed a p–n diblock concept and obtained a series of p–n diblock conjugated polymers.[3] The variation in p and n segments of the block polymer chain gave the possibility of tuning the HOMO and LUMO energy levels as well as emissive wavelengths. These polymers showed improved photoluminescent and electroluminescent properties. However, the improvement is still below the expected level. The poor improvement maybe attributed to the alternated distribution of the p-segment and n-segment in the polymer chain. Electron deficient unit inserted into a p-type polymer chain will partially act as the hole-blocking unit due to its high electron deficiency. Vice versa, the hole-transporting unit will lower the electron mobility.

The above-mentioned drawback can be resolved by defining the diblock oligomer with two separate blocks, the p-type and n-type unit, respectively. By tuning the unit length, the HOMO and LUMO energy levels can be accurately adjusted and controlled. In this letter, a series of diblock oligomers (**T_2O**, **T_2O_2**, and **T_4O_2**) consisting of electron-rich thiophene unit and electron-deficient oxadiazole unit with different unit lengths were successfully synthesized (Scheme 1). By changing number of thiophene and oxadiazole repeating units, the redox properties and emissive wavelength of those diblock oligomers were readily tuned. For comparison, another



Scheme 1. The structures of oligomers.

Keywords: Thiophene; Oxadiazole; Diblock oligomers; Triblock oligomers; Electronic properties.
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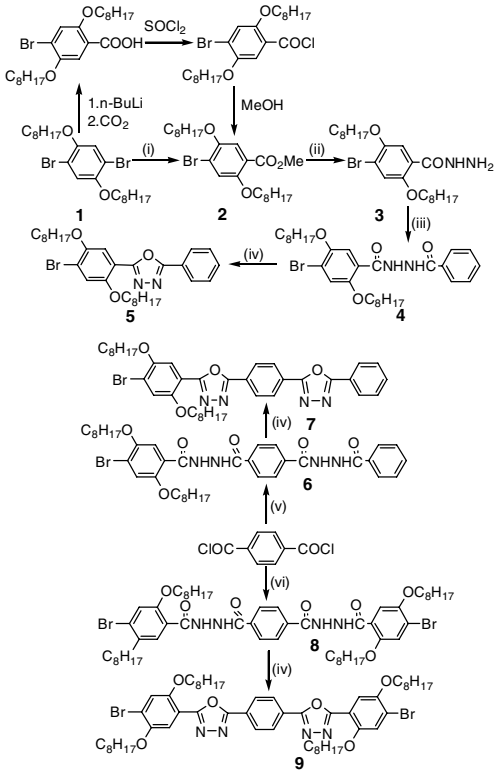
series of n–p–n(**OT_2O**) and p–n–p(**$T_2O_2T_2$**) triblock oligomers were also synthesized (Scheme 1). Comparing with the conjugated copolymers, the monodisperse conjugated oligomers possess well-defined and uniform structures, ease of purification and characterization.[4] Furthermore, deep electron traps possibly occur in polymeric systems due to chain entanglements or structural defects, which may not be observed in the well-defined oligomeric system.[5]

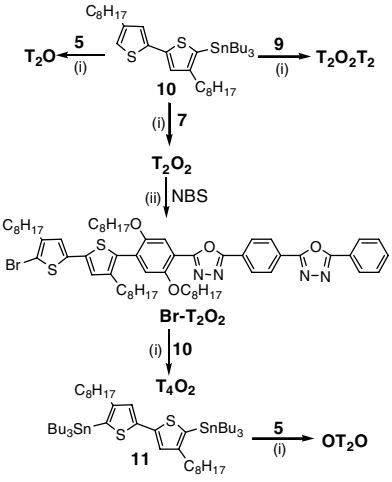
Generally, the oligomers synthesis involves three procedures, for example, the synthesis of the thiophene monomers, the synthesis of the oxadiazole monomers, and coupling reaction. Scheme 2 shows the synthetic route to oxadiazole monomer. The common synthetic sequence of 4-bromo-2,5-bis(octyloxy)benzoic acid methyl ester **2** from compound **1** involves three steps, which is rather complicated (Scheme 2). We developed a one-pot synthesis route for compound **2** from 1,4-dibromo-bis(octyloxy)benzene **1**. Compound **2** with 60% yield was prepared by treating **1** with *n*-BuLi and liquid dimethyl carbonate, which is more convenient to use than gas CO_2. Moreover, the monobromo-substituted oxadiazole dimer was synthesized successfully (Scheme 2). To the our best knowledge, no monobromo-substituted oxadiazole dimer has been synthesized so far. To obtain compound **6**, the mixture of compound **3** and benzohydrazide in pyridine was added into the solution of terephthaloyl dichloride in anhydrous THF slowly by a syringe. Compound **6** was obtained in 45% yield after the two by-products were removed by a silica gel chromatography. After cyclodehydration of Compound **6**, monobromo-substituted oxadiazole dimer **7** was obtained with 73% yield. The thiophene monomers **10** and **11** were prepared through the ordinary route.

Scheme 3 shows the synthetic route to the oligomers. The oligomers were constructed in moderate yield from the thiophene monomer with corresponding oxadiazole monomer by Stille reaction. Exceptably, due to the difficulty of obtaining pure monobromo-substituted tetrathiophene monomer through the ordinary route, **T_4O_2** was obtained from the Stille reaction of the stannane **10** with compound **Br–T_2O_2**, which was obtained by the bromination of **T_2O_2** with NBS. The structure and purity of all oligomers were verified by ^1H and ^{13}C NMR, MALDI-TOF-mass, and the elemental analysis.[6]

Spectroscopic properties of the oligomers were investigated with the UV–vis absorption and fluorescence emission. Figure 1a shows the absorption spectra of the oligomers in toluene. The oligomers, **T_2O_2**, **T_4O_2**,



Scheme 2. Reagents and conditions: (i) *n*-BuLi, −78 °C, Me_2CO_3, THF, 60%; (ii) $NH_2NH_2{\cdot}H_2O$, MeOH, 83%; (iii) benzoyl chloride, pyridine, 73%; (iv) $POCl_3$, 80 °C, 75% (**5**), 73% (**7**); (v) the solution of **3** and benzohydrazide in pyridine, THF, 45%; (vi) **3**, pyridine.



Scheme 3. Reagents and conditions: (i) $Pd(PPh_3)_4$ (3%), 100 °C, toluene, 60% (**T_2O**), 71% (**T_2O_2**), 73% (**T_4O_2**), 70% (**OT_2O**), 35% (**$T_2O_2T_2$**); (ii) NBS, $CHCl_3$/AcOH, 80%.

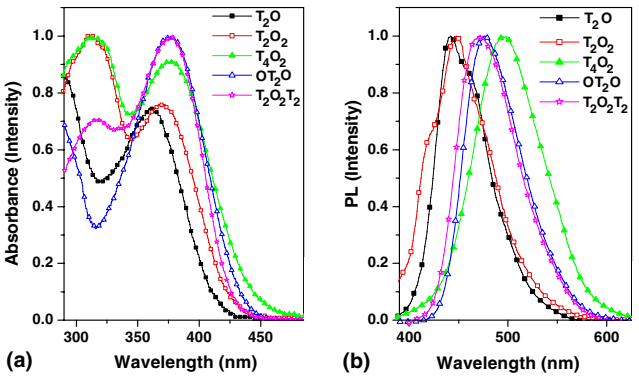


Figure 1. (a) Absorption spectra in toluene, (b) fluorescence spectra in toluene (1×10^{-5} M solution in toluene, normalized).

and **$T_2O_2T_2$** show two distinct absorption bands. The absorption bands at longer wavelength range (>360 nm) come from the thiophene units,[7] and the remarkable enhancement of the absorption intensity of **T_4O_2** relative to **T_2O_2** reflects the corresponding increases in the number of thiophene units in the oligomers. Another absorption bands of **T_2O_2**, **T_4O_2**, and **$T_2O_2T_2$** (around 300 nm) come from the π–π^* transition of oxadiazole groups.[8] This implies that the electronic interactions between the oxadiazole units and thiophene units are rather limited. Nevertheless, both **T_2O** and **OT_2O** display no remarkable absorption band in the range of shorter wavelengths.

Figure 1b shows the normalized fluorescence emission spectra of the oligomers in toluene. In the case of diblock oligomers, with the increasing number of thiophene unit in **T_4O_2** relative to **T_2O_2**, bathochromic shifts result from the formation of a highly extended π-delocalized system.

T_4O_2 versus **$T_2O_2T_2$** and **T_2O_2** versus **OT_2O** with different regiochemistry exhibit different emission wavelength in spite of the same unit numbers. Apparently, the emission wavelength can be modulated by different molecular regiochemistry as well as unit number. The emissive color varying from blue to green were achieved for the respective toluene solutions.

All of the oligomers exhibit only one maximum emission, and this emission maximum is clearly independent to the excitation wavelength. This indicates the existence of efficient energy transfer from the oxadiazole moiety to the thiophene chromophore.[8a] The PL quantum yield (Φ_f) of **T_2O**, **T_2O_2**, and **OT_2O** were calibrated against 9,10-diphenylanthracene (Table 1). They were remarkably higher than that of poly(3-octylthiophene) ($\Phi = 0.11$).

Table 1. Optical properties of the oligomers

Oligomer	Abλ_{max}[a] (nm)	PLλ_{max}[a] (nm)	Φ_f[b] (%)
T_2O	/363	441	16
T_2O_2	312/371	446	19
T_4O_2	314/377	495	
OT_2O	/376	471	17.5
$T_2O_2T_2$	315/376	451	

[a] Measured in toluene (1×10^{-5} M).
[b] 9,10-Diphenylanthracene standard ($\Phi_{PL} = 0.95$ in cyclohexane).

The redox properties of these materials were determined by cyclic voltammetry in the CH_2C1_2 and THF solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) using a Pt wire as a counter electrode and a $Ag/AgNO_3$ (0.1 M) electrode as the reference electrode. When scanning cathodically, all oligomers display reversible reduction processes. In the case of the diblock oligomers, the increase of the oxadiazole ring number in the oxadiazole unit changes the reduction potential of those material remarkably ($E^{1/2(R)}_{T_2O_2} = -2.06$ V and $E^{1/2(R)}_{T_2O} = -2.44$ V versus Ag/Ag^+). The detailed data are listed in Table 2 and cyclic voltammograms are given in Figure 2. The increasing thiophene ring number of those materials does not affect the reduction potential remarkably. As seen from Figure 2 and Table 2, the introduction of one oxadiazole ring to the terminal thiophene side of **T_2O** (**$T_2O \rightarrow OT_2O$**) had much smaller effect to the terminal oxadiazole side (**$T_2O \rightarrow T_2O_2$**) regarding the reduction potential ($E^{1/2(R)}_{T_2O_2} = -2.06$ V and $E^{1/2(R)}_{OT_2O} = -2.39$ V versus Ag/Ag^+). The molecular regiochemistry has also a significant impact on the reduction potential ($E^{1/2(R)}_{T_2O_2} = -2.06$ V and $E^{1/2(R)}_{OT_2O} = 2.39$ V versus Ag/Ag^+). This finding points out the existence of electronic interaction between two adjacent oxadiazole rings. Cyclic voltammetric reduction potential values can be used as a surrogate for LUMO energy levels. The results suggest that the LUMO of those molecules can be effectively adjusted by changing the oxadiazole ring number and molecular regiochemistry. The reduction onset potential of **T_2O_2** and **T_4O_2** was measured to be -1.98 and -2.00 V versus Ag/Ag^+. The value is comparable with that of 1,3,5-tris(*N*-phenylbenzimidizol-2-yl)benzene (**TPBI**) (-1.7 V versus SCE), one of the most widely used electron-transporting materials.[9]

On sweeping anodically, all of those materials undergo a reversible multielectron (two or three) oxidation originating from oligothiophene segments except **$T_2O_2T_2$**. Unlike their reduction potentials, the oxidation potential of diblock oligomers is sensitive to the variation of thiophene ring number in the oligothiophene units ($E^{1/2(O)}_{T_2O_2} = 0.65$ V and $E^{1/2(O)}_{T_4O_2} = 0.52$ V versus Ag/Ag^+), while the increase of oxadiazole ring does not change the oxidation potentials ($E^{1/2(O)}_{T_2O} = 0.67$ V versus Ag/Ag^+) remarkably. This indicated that the HOMO level of the diblock oligomers can be effectively adjusted by

Table 2. Electrochemical data of oligomers

Oligomer	Reduction[a]	Oxidation[a]	LUMO/HOMO[c] (eV)
	E_{pa}/E_{pc}[b] (V)	E_{pc}/E_{pa} (V)	
T_2O	−2.52/−2.36	0.83/0.52	−2.37/−5.37
T_2O_2	−2.13/−1.99	0.78/0.52	−2.72/−5.39
T_4O_2	−2.13/−2.03	0.61/0.44	−2.70/−5.15
OT_2O	−2.51/−2.28	0.76/0.64	−2.40/−5.30
$T_2O_2T_2$	−2.32/−2.16	0.83/0.72	−2.60/−5.38

[a] Determined by cyclic voltammetry in dichloromethane (for oxidation) and THF (for reduction) with $Ag/AgNO_3$ (0.1 M) as a reference electrode. Scan rate: 200 mV s^{-1}.
[b] E_{pa} and E_{pc} stand for anodic peak potential, and cathodic peak potential, respectively.
[c] HOMO and LUMO energy was calculated with reference to ferrocene (4.7 eV).

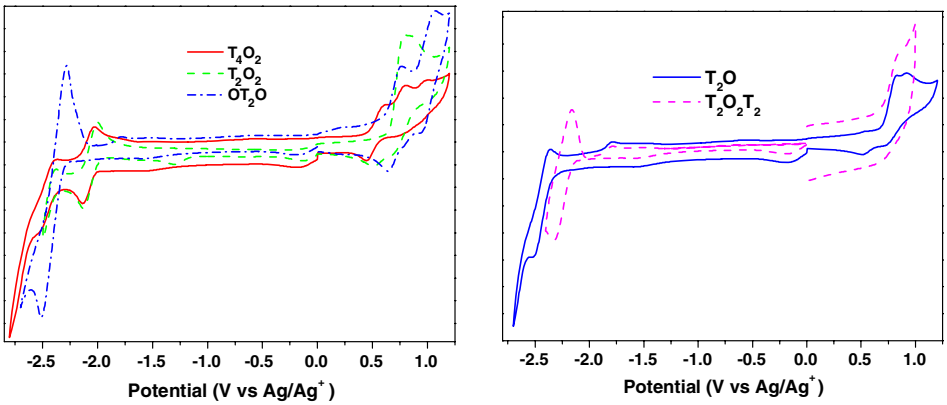


Figure 2. Cyclic voltammogram of oligomers. Measured in dichloromethane (for oxidation) and THF (for reduction). Scan rate: 200 mV s^{-1}.

changing the thiophene number. In the same way, the oxidation potential can also be drastically modulated by changing the molecular regiochemistry ($E^{1/2(O)}_{T_4O_2}$ = 0.52 V and $E^{1/2(O)}_{T_2O_2T_2}$ = 0.77 V versus Ag/Ag^+).

All oligomers undergo both reversible oxidation and reduction process except **$T_2O_2T_2$**, suggesting their potential bipolar charge transport properties.[10] Molecules that can stabilize both cation and anion radicals are suggested to be beneficial for OLED devices.[11] However, most of the respective diblock copolymers showed irreversible oxidation process.[3]

In conclusion, a new series of p–n diblock and triblock oligomers were synthesized and characterized. Changing the number of thiophene and oxadiazole ring of the diblock oligomer can modulate the redox behavior and emission wavelength. We also made interesting findings on the effect of molecular regiochemistry to electronic properties. These should be valuable for the molecule design of other organic electronic materials besides light-emitting materials.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.001.

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6. Physical data for oligomers. **T_2O**: ^{1}HNMR (400 MHz, $CDCl_3$): δ 8.18–8.16 (d, 2H), 7.70 (s, 1H), 7.58–7.52 (m, 4H), 7.04 (s, 1H), 7.02 (s, 2H), 6.80 (s, 1H), 4.10–4.07 (t, 2H), 4.05–4.01 (t, 2H), 2.61–2.48 (m, 4H), 1.92–1.84 (m, 2H), 1.76–1.69 (m, 2H), 1.63–1.58 (m, 8H), 1.39–1.18 (m, 40H), 0.90–0.82 (m, 12H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.0, 164.0, 151.1, 150.8, 144.4, 142.0, 137.3, 137.2, 131.7, 131.3, 129.2, 128.6, 127.1, 125.2, 125.0, 124.5, 119.0, 117.4, 114.3, 112.9, 69.9, 69.7, 32.1, 32.0, 30.8, 30.7, 30.6, 29.9, 29.7, 29.6, 29.5, 29.4, 26.5, 26.2, 22.9, 14.3 ppm. Anal. Calcd for $C_{54}H_{78}N_2O_3S_2$: C, 74.78; H, 9.06; N, 3.23; S, 7.39. Found: C, 74.73; H, 9.10; N, 3.27; S, 7.33. MS (MALDI-TOF): 865.9 (calcd for $C_{54}H_{78}N_2O_3S_2$: 866.5). **T_2O_2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 4H), 8.19–8.17 (d, 2H), 7.72 (s, 1H), 7.59–7.56 (m, 3H), 7.04–7.01 (t, 3H), 6.80 (s, 1H), 4.11–4.08 (t, 2H), 4.03–4.00 (t, 2H), 2.60–2.51 (m, 4H), 1.93–1.89 (t, 2H), 1.76–1.72 (t, 2H), 1.62–1.58 (m, 8H), 1.54–1.25 (m, 40H), 0.90–0.82 (m, 12H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.2, 164.5, 164.1, 164.0, 151.2, 150.8, 144.3, 142.0, 137.3, 137.2, 132.2, 131.2, 129.4, 129.0, 127.7, 127.6, 127.3, 127.2, 126.6, 125.5, 125.0, 123.8, 119.1, 117.3, 114.3, 112.4, 69.9, 69.7, 34.0, 32.1, 32.1, 32.0, 30.8, 30.7, 30.6, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 26.5, 26.2, 22.9, 14.3 ppm. Anal. Calcd for $C_{62}H_{82}N_4O_4S_2$: C, 73.62; H, 8.17; N, 5.54; S, 6.34. Found: C, 73.58; H, 8.22; N, 5.49; S, 6.29. MS (MALDI-TOF): 1010.4 (calcd for $C_{62}H_{82}N_4O_4S_2$: 1010.58). **T_4O_2**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 4H), 8.18–8.17 (d, 2H), 7.72 (s, 1H), 7.58–7.56 (t, 3H), 7.04–6.99 (m, 4H), 6.86 (s, 1H), 4.11–4.08 (t, 2H), 4.04–4.01 (t, 2H), 2.56–2.50 (m, 8H), 1.91–1.89 (t, 2H), 1.76–1.72 (t, 2H), 1.61–1.56 (m, 20H), 1.42–1.25 (m, 60H), 0.93–0.82 (m, 18H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.2, 164.5, 164.1, 164.0, 163.9, 151.2, 151.1, 144.3, 143.5, 143.4, 142.2, 137.6, 137.2, 137.1, 136.8, 132.2, 131.4, 129.4, 128.9, 127.7, 127.6, 127.5, 127.2, 127.0, 126.6, 125.3, 125.1, 123.8, 119.2, 117.3, 114.3, 112.5, 109.4, 69.9, 69.7, 34.0, 32.2, 32.1, 32.0, 31.8, 31.6, 30.8,

30.7, 30.6, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.2, 28.0, 27.9, 27.4, 27.1, 26.7, 26.5, 26.3, 22.9, 19.4, 17.7, 14.3, 13.8 ppm. Anal. Calcd for $C_{86}H_{118}N_4O_4S_4$: C, 73.77; H, 8.49; N, 4.00; S, 9.16. Found: C, 73.75, H, 8.53; N, 3.97; S, 9.12. MS (MALDI-TOF): 1399.1 (calcd for $C_{86}H_{118}N_4O_4S_4$: 1398.8). **OT_2O**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16–8.14 (d, 4H), 7.70 (s, 2H), 7.54–7.52 (m, 6H), 7.06 (s, 2H), 7.02 (s, 2H), 4.10–4.06 (t, 4H), 4.03–4.00 (t, 4H), 2.55–2.51 (t, 4H), 1.90–1.86 (t, 4H), 1.76–1.72 (t, 4H), 1.65–1.52 (m, 12H), 1.41–1.23 (m, 60H), 0.90–0.83 (m, 18H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.0, 164.0, 151.1, 150.8, 142.1, 136.9, 131.7, 131.5, 129.2, 128.6, 127.1, 125.2, 124.5, 117.4, 114.3, 112.9, 69.9, 69.7, 60.6, 32.1, 32.0, 30.8, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 28.0, 27.0, 26.5, 26.2, 22.9, 17.7, 14.4, 14.3, 13.8 ppm. Anal. Calcd for $C_{84}H_{118}N_4O_6S_2$: C, 75.07; H, 8.85; N, 4.17; S, 4.77. Found: C, 74.04; H, 8.90; N, 4.11; S, 4.73. MS (MALDI-TOF): 1344.1 (calcd for $C_{84}H_{118}N_4O_6S_2$: 1342.8). **$T_2O_2T_2$**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 4H), 7.71 (s, 2H), 7.04–6.98 (m, 6H), 6.80 (s, 2H), 4.11–4.08 (t, 4H), 4.03–4.00 (t, 4H), 2.60–2.51 (m, 8H), 1.93–1.89 (m, 4H), 1.76–1.72 (m, 4H), 1.63–1.53 (m, 16H), 1.41–1.00 (m, 80H), 0.90–0.77 (m, 24H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): δ 165.2, 164.2, 164.1, 151.7, 150.0, 144.3, 142.0, 137.3, 137.2, 132.2, 131.2, 129.4, 129.0, 127.6, 127.4, 127.3, 126.9, 126.6, 125.2, 125.0, 123.8, 118.9, 117.8, 114.4, 112.4, 69.9, 69.7, 32.0, 29.6, 29.5, 29.4, 29.3, 26.3, 26.2, 22.9, 22.8, 14.3 ppm. Anal. Calcd for $C_{102}H_{150}N_4O_6S_4$: C, 73.95; H, 9.13; N, 3.38; S, 7.74. Found: C, 73.91; H, 9.09; N, 3.34; S, 7.68. MS (MALDI-TOF): 1656.6 (calcd for $C_{102}H_{150}N_4O_6S_4$: 1655.0).

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